-3) Knudd. Serie: Hydrog.

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KØBENHAVN
I KOMMISSION HOS C. A. REITZEL
BIANCO LUNOS BOGTRYKKERI
1904

MEDDELELSER

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KOMMISSIONEN FOR HAVUNDERSØGELSER

SERIE: HYDROGRAFI

BIND I

KOMMISSIONEN FOR HAVUNDERSØGELSER (The Danish Committee for the Study of the Sea) is appointed by LANDBRUGSMINISTERIET (the Danish Board of Agriculture) with the duty to carry out the Danish part of work to be done in the INTERNATIONAL COOPERATION FOR THE STUDY OF THE SEA. The Committee consists of the undersigned four members.

Dr. phil. C. G. JOH. PETERSEN is the Chairman and the Director of the Fisheries Investigations carried out by the Committee. Havnekapitain C. F. DRECHSEL is specially charged with the equipment and management of the researchsteamer "Thor". Docent MARTIN KNUDSEN is Secretary to the Committee and Director of the Hydrographic Investigations. Museumsinspektør C. H. OSTENFELD is Director of the Plankton Investigations. The Committee intends to publish its Reports (Meddelelser) in three series, that is to say Serie: Fiskeri, Serie: Plankton and Serie: Hydrografi. These Reports are to be issued in 4to either in the English or in the German language. Some occasional papers (Skrifter) are to be issued in 8vo and printed in Danish.

August 1904

C. F. DRECHSEL

C. G. JOH. PETERSEN
Chairman

C. H. OSTENFELD

MARTIN KNUDSEN
Secretary

MEDDELELSER FRA KOMMISSIONEN FOR HAVUNDERSØGELSER
SERIE: HYDROGRAFI · BIND I · NR. 1 1904

ON THE ORGANISATION

OF

THE DANISH HYDROGRAPHIC RESEARCHES

BY

MARTIN KNUDSEN

KØBENHAVN
I KOMMISSION HOS C. A. REITZEL
BIANCO LUNOS BOGTRYKKERI
1904

In the years 1883—86 a series of hydrographic observations was undertaken from Fiskeriinspektionsskibet "Hauch" by C. F. DREHSEL and Dr. C. G. JOH. PETERSEN[1]). In 1891 a new series was undertaken by C. F. WANDEL, at that time director of the Hydrographic Department, and the researches were continued during the following years also under his direction. At about 60 different places in the Kattegat, the Belts, the Sound, and the western part of the Baltic observations of temperature and salinity were taken in different depths, 4 times each year, viz. February 1st, May 1st, August 1st and November 1st. In order to work up these observations, a commission was appointed 1893 (Kommissionen for videnskabelig Undersøgelse af de danske Farvande), and this commission entrusted the publishing and discussion of the observations during the years 1891, 1892 and 1893 to Dr. K. RØRDAM[2]).

In the following years after 1893 periodical observations were taken at the same dates as before, but the number of the places for observations (stations) could not be kept without diminishing; it grew less and less until the year 1902. Some of these observations were published and the results discussed by MARTIN KNUDSEN[3]).

In the year 1897 observations of temperature and salinity were started by C. F. WANDEL in the waters by the Faroe islands and Iceland. Only surface observations and Plankton collections could be made and only the results for the years 1897, 1898 and 1899 have just been published[4]).

During the year 1899 and 1900 a series of laboratory investigations was undertaken in order to determine the relations between chlorine, specific gravity and salinity of the sea water[5]).

In the year 1899 the Danish Government sent delegates to an international conference in Stockholm and after that appointed a committee to make proposals about the way in which Denmark ought to take part in the international cooperation for the study of the sea on the basis of the programme, worked out by the conference in Stockholm. In 1901 Danish delegates also attended a second conference held in Kristiania, and in the year 1902 the international investigations were started. In order to take

[1]) Det videnskabelige Udbytte af Kanonbaaden „Hauch"s Togter i de danske Have indenfor Skagen i Aarene 1883—86. Ved C. G. JOH. PETERSEN. København 1893.

[2]) Beretning fra Kommissionen for videnskabelig Undersøgelse af de danske Farvande. Bind 1. Hefte 1 og 2. København 1896.

[3]) Beretning fra Kommissionen for videnskabelig Undersøgelse af de danske Farvande. Bind 2. Hefte 1—3. København 1897, 1899 and 1900.

[4]) Iagttagelser over Overfladevandets Temperatur, Saltholdighed og Plankton paa islandske og grønlandske Skibsrouter i 1897 af C. F. WANDEL og C. OSTENFELD. København 1898.

Iagttagelser over Overfladevandets Temperatur, Saltholdighed og Plankton paa islandske og grønlandske Skibsrouter i 1898 foretagne under Ledelse af C. F. WANDEL bearbejdede af MARTIN KNUDSEN og C. OSTENFELD. København 1899.

And a similar paper for the year 1899. (København 1900.)

[5]) Hydrographical tables by MARTIN KNUDSEN. København 1901.

Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen von CARL FORCH, MARTIN KNUDSEN und S. P. L. SØRENSEN. Gesammelt von MARTIN KNUDSEN. D. Kgl. Danske Vidensk. Selsk. Skr., 6. Række, naturvidensk. og mathem. Afd. XII. 1. København 1902.

Berichte über die chemische und physikalische Untersuchung des Seewassers und die Aufstellung der neuen Hydrographischen Tabellen von MARTIN KNUDSEN, CARL FORCH und S. P. L. SØRENSEN. Wissenschaftliche Meeresuntersuchungen, herausgegeben von der Kommission zur Untersuchung der deutschen Meere in Kiel und der Biologischen Anstalt auf Helgoland. Abtheilung Kiel. Neue Folge. Band 6. Kiel 1902.

part in these investigations, the Danish Government and Parliament granted a sum af 173000 Kr. for the starting and 100000 Kr. yearly in 3 years, and resolved that the investigations should be carried out under the direction of the Department of Agriculture by a committee consisting of 4 members (Kommissionen for Havundersøgelser). The members of the committee divided the duties among themselves in the following way: Dr. C. G. Joh. Petersen, the chairman of the committee, became director of the fishery investigations, Havnecapitain C. F. Drechsel was specially charged with the equipement of the investigation steamer "Thor", Musæumsinspektør C. H. Ostenfeld became director of the Plankton investigations, and Docent ved Universitetet Martin Knudsen became director of the hydrographic investigations.

In order to carry out the hydrographic researches according to the programme of the conferences in Stockholm and Kristiania and the instructions laid down by the "International Council for the Study of the Sea", rooms were hired in Copenhagen for a hydrographical laboratory, and Magister H. J. Hansen was appointed assistant at this laboratory. (Now the assistant is cand. mag. J. P. Jacobsen). To carry out the hydrographical investigations on board the investigation steamer "Thor" cand. mag. J. N. Nielsen was appointed.

As the means granted for the investigations were not sufficient to keep the investigation steamer "Thor" in activity throughout the year, it was resolved that the hydrographical investigations by the Faroe islands and Iceland should be limited to the months of May and August, and that in the other months in which it could be kept in work, the ship should be used for fishery investigations, partly at the Faroe islands and Iceland, and partly in the waters surrounding Denmark.

The investigation steamer "Thor" is furnished with a laboratory, in which the ordinary titrations and gasanalyses are carried out together with other small hydrographic experiments and measurements. The steamer is also furnished with a small steam winch and a hand winch to take up water samples, and to take observations of temperatures in the depth.

In May and August 1903 the hydrographic researches were carried out in accordance with the instructions given to the hydrographer Mr. J. N. Nielsen. Hydrographic observations should be taken at the following 19 stations, lying on the top and on both sides of the ridge between the Faroe islands and Iceland:

Name of the station	N Lat.	W Long.	Depth Meter	Name of the station	N Lat.	W Long.	Depth Meter
Da Atl 1	61°35′	4°39′	400	Da Atl 11	64°05′	9°38′	600
— — 2	62°34′	6°20′	250	— — 12	63°40′	10°38′	500
— — 3	63°06′	6°20′	1300	— — 13	63°12′	11°45′	500
— — 4	63°33′	6°20′	1800	— — 14	63°43′	11°45′	550
— — 5	63°10′	7°31′	1100	— — 15	64°12′	11°45′	450
— — 6	62°40′	8°44′	400	— — 16	64°35′	11°45′	400
— — 7	62°12′	9°56′	800	— — 17	64°58′	11°45′	500
— — 8	63°03′	9°28′	500	— — 18	64°58′	12°40′	200
— — 9	63°50′	9°00′	600	— — 19	64°58′	13°25′	100
— — 10	64°26′	8°37′	1100				

In order to save time for the fishery investigations, the hydrographer was instructed to finish the work as quickly as possible, and at all events not to use more than 30 days (now 25 days) for the cruise. If he found, that extra stations were urgently necessary to get the whole hydrographic situation, he was allowed to take some, if it could be done without exceeding the maximum time mentioned above. The observations should be carried out according to the rules given by the conference, and the circulars issued by the international bureau of the council.

During the time in which the fishery investigation was going on, the hydrographer should use every opportunity to get informations about the hydrography, and at all places where fishery was going on, hydrographic observations should be taken.

The hydrographic observations and the results of the analyses were sent to the Hydrographic Laboratory, and the part of them which should be sent to the international bureau, was entered in the schemes forwarded by that bureau, and sent in. This part of the observations is published in: "Bulletin des résultats acquis pendant les courses périodiques publié par le Bureau du Conseil avec l'assistance de M. KNUDSEN", and will not be published again in these papers: "Meddelelser fra Kommissionen for Havundersøgelser".

At the conference in Stockholm it was left to Denmark to undertake the seasonal cruises, not only in the waters by the Faroe islands and Iceland, but also in the Kattegat and the Great Belt. As stated above, the cruises by the Faroe islands and Iceland are undertaken by the investigation steamer "Thor", and therefore other arrangements must be made to undertake the investigations in the Kattegat and the Great Belt. In these waters the cruises are made in all the four typical months: February, May, August and November, by means of 3 steamers, of which the two belong to the Royal Danish Navy, and one to the Department of Agriculture. The two first mentioned ships have mostly been "Vagerinspektionsskibet Løvenørn", Captain Bay Smith, and "Fyrinspektionsskibet C. F. Grove", Captain Saxild; the last mentioned ship was "Fiskerikontroldamperen Falken", Captain Holstein and lately Captain MORTENSEN. By means af these 3 ships, the investigations of the Kattegat and the Great Belt only take 2—3 days. The "Løvenørn" has the northern part, the "C. F. Grove" the southern part of the Kattegat, and the "Falken" the Great Belt to investigate. The investigations are carried out at the following 32 stations:

Name of the station	N Lat.	E Long.	Name of the station	N Lat.	E Long.
Da 1 close to the light-ship: Skagens Rev			Da 17	57°01'2	11°40'4
— 2	57°47'5	10°52'0	— 18	56°47'3	11°47'0
— 3	57°51'4	10°46'3	— 19	56°35'4	11°51'3
— 4	57°57'7	10°49'6	— 20	56°22'3	11°48'6
— 5	57°55'3	11°05'3	— 21	56°07'9	11°11'1
— 6	57°49'8	11°05'4	— 22	55°56'9	11°00'2
— 7	57°52'0	11°18'0	— 23	55°46'7	10°48'8
— 8	57°52'7	11°22'2	— 24	55°36'6	10°48'8
— 9	57°41'0	11°23'0	— 25	55°29'8	10°52'6
— 10	57°35'6	11°29'8	— 26	55°20'4	11°02'3
— 11	57°33'1	11°23'5	— 27	55°19'2	10°53'4
— 12	57°24'8	10°48'0	— 28	55°11'9	11°05'3
— 13	57°25'3	10°41'2	— 29	55°01'5	11°02'2
— 14	57°20'0	11°30'8	— 30	54°52'5	10°50'5
— 15	57°17'9	11°27'4	— 31	53°43'9	10°46'4
— 16	57°08'6	11°25'6	— 32	54°35'5	11°03'5

Of these stations the southermost in the Femer Bælt, Da 32, is lying at the same place as the German station D Ostsee 3; Da 23 in the northern part of the Great Belt is worked twice at each cruise, by the "Falken" and by the "C. F. Grove", and Da 10, south west of Vinga, is also worked twice, being taken both by the "C. F. Grove" and by the "Løvenørn"; the station Da 9 is lying at the same place as the Swedish station S Skag 0. This repetition of the stations is done in order to see, how much the hydrographic situation is able to alter within a short time.

The observations on board these 3 ships are carried out by observers, specially sent out for the purpose. The assistant at the laboratory, Magister H. J. HANSEN, ordinarily makes the cruise with the "Falken", and Mr. OSTENFELD makes the cruise with one of the other ships. The cruises with the third ship have in some cases been made by Mr. H. RAVN, director of the nautical department of the Meteorological Institute, in other cases by the chemist Magister N. BJERRUM, in order to try his new method for the determination of oxygen in the sea water.

The water samples collected during these cruises are stored in small glassbottles, and afterwards analysed in the Hydrographic Laboratory, where also the observations are worked out and prepared for the sending in to the international bureau.

In order to follow to a certain extent the hydrographic variations, that take place between the seasonal cruises, observations of the temperature of the surface water are taken, and water samples from the surface collected by the following ships:

Name of the Ship	Owner	Captain	Observer	Voyage		Mean number of samples from each voyage	Total number of samples from October 1902 to April 1904
				from	to		
S/s "Laura"	Det forenede Dampskibs-selskab	J. F. Aasberg	Styrm. P. Larsen — Carlslund — Egense	København	Island	40	479
S/s "Vesta"	—	Th. Godtfredsen	— L. D. Lydersen	—	—	39	270
S/s "Ceres"	—	A. R. da Cunha	— J. A. Strufve	—	—	38	188
S/s "Botnia"	—	H. Bønnelykke	— F. Hansen	—	—	38	38
S/s "Holar"	—	P. Østjacobsen	— A. H. Swan	Reykjavik (Øst om Island)	Øfjord	—	76
S/s "Baldur"	—	J. C. P. Hardt	— P. V. Frandsen	Larvig	Frederiksh.	20	140
S/s "Blenda"	—	Bonnesen	— J. Petersen	Frederiksh.	Gøteborg	11	77
S/s "N. J. Fjord"	—	Mecklenburg	— Chr. Rasmussen	Esbjerg	Parkeston	20	80
S/s "Mjølnir"	Dampskibsselskabet "Tore"	Hendersen	— S. M. Kirch — H. C. Marker	København	Island	41	287
S/s "Godthaab"	Kgl. grønlandske Handel	H. V. Bang	— Kjøller — Hansen	—	Grønland	50	148
"Nordlyset"	—	C. W. Søeby	— H. Th. Jørgensen — Jul. Hansen	—	—	64	128
"Ceres"	—	O. Pedersen	Fører O. Petersen	—	—	54	54
"Constance"	—	J. Stoklund	Styrm. J. Gaarn Pedersen	—	—	53	53
"Tjalfe"	—	B. Rickmert	— N. P. Sørensen	—	—	54	54
						total	2072

These water samples are titrated in the Hydrographic Laboratory, as well as the water samples from the light-ships.

At the following light-ships:

Horns-Rev
Vyl
Skagens-Rev
Læsø-Trindel
Læsø-Rende
Kobbergrund
Anholt-Knob
Schultz's-Grund
Lappe-Grund
Drogden
Gjedser-Rev

temperature and salinity of the water at different depths are determined once every day for the Meteorological Institute, and the results published by the institute in "The Nautical Meteorological Annual". As the salinities can only be determined on board the light-ships by means of hydrometers, a cooperation between the Meteorological Institute and the Hydrographic Laboratory is established in the following way. From some of the light-ships water samples are taken from different depths twice a week and sent to the Hydrographic Laboratory for titration. From Horns-Rev samples are taken in the depths of 0, 10, 20 and 28 Meters, from Skagens-Rev in the depths of 0, 10, 20 and 38 Meters, from Læsø-Rende in the depths of 0 and 21 Meters, from Kobbergrund in the depths of 0 and 17 Meters, and from the light-ships Anholt-Knob, Schultz's-Grund, Lappegrund and Gjedser-Rev samples only are taken from the bottom.

In order to control the hydrometer determinations, the results of all these titrations (ca. 1600 a year) together with the corresponding hydrometer determinations are published in the Nautical Meteorological Annual, edited by the Danish Meteorological Institute.

The number of titrations executed in the Hydrogrophic Laboratory amount to about 4000 a year. To do all these titrations and take care of the instruments to be used on board and provide the water samples from the ships, would take a man's whole time and leave no time for scientific work. The assistant therefore does not do the titrations himself, he only has to control them, to be sure that no systematic error arises, which may be avoided. The titrations are all done by Miss P. HEDEGAARD.

Of the scientific work done in the Hydrographic Laboratory I only shall mention, what has been finished now. The assistant at the laboratory, Magister H. J. HANSEN, has undertaken a series of determinations of the freezing-points of different water samples and the corresponding specific gravities, to get the relation between freezing-point, specific gravity, chlorine and salinity. The chemist Mr. N. BJERRUM who has also worked for the laboratory, has made some researches on the systematic errors, which arise by an ordinary titration, in order to show, how to get the greatest exactitude without increasing the work spent on a titration, and to give information about the influence of each single of the errors and the value of the mean error.

520 29/VIII 1904.

MEDDELELSER FRA KOMMISSIONEN FOR HAVUNDERSØGELSER
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EXPERIMENTAL DETERMINATION

OF THE RELATION BETWEEN

THE FREEZING POINT OF SEA-WATER

AND ITS SPECIFIC GRAVITY AT 0° C.

BY

H. J. HANSEN

KØBENHAVN
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1904

1. The Watersamples.

The watersamples applied in these determinations were the same as applied by Mr. Martin Knudsen in the constant-determinations for the revision of the hydrographic tables. As to the collecting of the watersamples we, therefore, refer to Martin Knudsen[1]): Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen pag. 17—22. They were, as stated in the above mentioned paper, kept in 6-liter bottles of common green bottleglass. The bottle was closed by a cork through which two glasstubes were passing, one of them went down to the bottom of the bottle while the other ended right beneath the cork. On the glasstubes were fixed indiarubber tubes, closed by clips, and the cork was sealed with a mixture of wax, colophony, and ferric oxide, so that it closed perfectly hermetically.

The water was always taken from the bottles by producing, by means of an indiarubber blower, quite a slight compression in the bottle, never by sucking, as then part of the water might evaporate, and so the concentration of it be altered.

The water which for a lengthened time had been kept in the glasstube which reached the bottom of the bottle, and in the indiarubber tube connected with this tube, was drawn and thrown away, as it might be feared to have a greater concentration than the water in the very bottle, partly on account of the crystals of salt deposited in the outermost part of the indiarubber tube, partly because it might have dissolved part of the glass.

2. Determinations of the Freezing Point.

The method used to determine the freezing point was the one stated by K. Prytz[2]). This method has several advantages preferable to the methods of determining the freezing point which are based on an undercooling of the solution. For by using Prytz's method the temperature keeps constant for a much longer time than by using the other methods. Besides, in this method, the temperature quickly approaches asymptotically to the real freezing point, and the temperature of the surroundings outside Dewar's vessel has no influence on its height, while the height of the freezing point in the methods based on an undercooling of the solution is dependent on the exchange of heat with the surroundings, on the alteration of concentration by the formation of ice, and on the heat produced by the stirring.

The apparatus was as shown in fig. 1.

In a Dewar's vessel, *A*, 20 cm. high and of a 5 cm. inside diameter, in which the surfaces turning to the vacuum are silvered, a Beckmann's thermometer divided in $^1/_{100}°$ is placed, round which is laid

[1]) D. kgl. danske Vidensk. Selsk. Skr., 6. Række. naturvidensk. og matem. Afd. XII. 1.

[2]) K. Prytz: Methode zur Bestimmung des Gefrierpunktes einer Lösung bei konstanter Temperatur. Ann. der Physik. 7, 1902. pag. 882.

a screwformed brasstube, *a*, called a brass-spiral, with 30 turns. The Dewar's vessel is supported by pieces of cork, *p*, and placed in a larger cylindrical vessel, which, besides keeping the Dewar's wessel perpendicular, also tends to gather the solution, which is, during the experiment, gradually flowing out of the Dewar's vessel. The brasstube which does not protrude from the vessel, that it may not conduct heat from the surroundings, ends a little below the bulb of the thermometer, and at the top a short indiarubber tube, *b*, and a glasstube connects it with another brasstube, *c*, which is placed in a vessel, *C*, made of a glass bottle, the bottom of which has been blasted away. In this vessel is placed a cooling bath, according to circumstances a mixture of water and snow, or a mixture of sea-water and snow, so that the fluid which is to be examined may be cooled as far as to its freezing point before it enters the spiral in the Dewar's vessel. The cooling bath is well wrapt up in cotton so that its temperature may more easily be kept pretty constant. The brassspiral, *c*, which has 10 turns with a diameter of 6 cm. is at the top by an indiarubber tube, *d*, supplied with a clip (which is not drawn in the figure), connected with a short glasstube which goes through an indiarubber stopper placed in the lower end of a glasstube, 7 cm. long and 2 cm. wide. Through an indiarubber stopper in the upper end of this glasstube is placed a vessel, *D*, supplied with two cocks. Into this vessel, the capacity of which is 320 cc., the sea-water is poured direct from the bottles in which it is kept. The different parts of the apparatus are held in their due places by means of an iron stand.

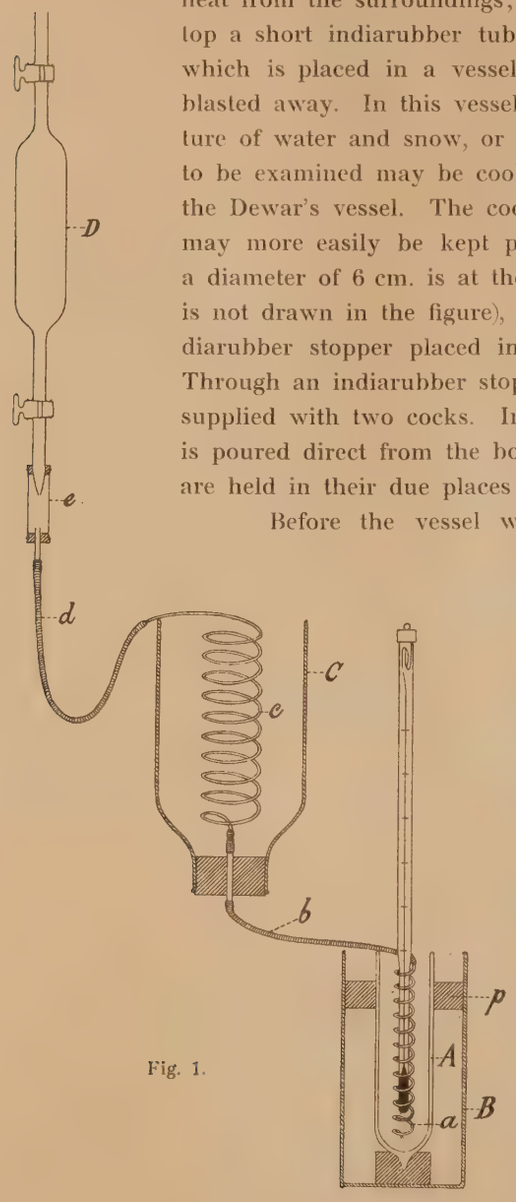

Fig. 1.

Before the vessel was filled with sea-water it was well rinsed with the water sample which had to be examined, and then it was half filled and put on its place in the apparatus; the cocks were opened, and now the water ran down through the indiarubber tube and the brasstubes and rinsed them. During the rinsing the brass spiral in the Dewar's wessel was taken out of it, and the thermometer was sunk in a mixture of snow and water to the division to which it was sunk when placed in the Dewar's vessel; the upper part of the thermometer being in the air. The intention with placing the thermometer thus was to avoid changes of its zero. So during the whole period of experiments great care was taken that its temperature was never above 0° C.; during the night it was placed in snow in the Dewar's vessel.

While the rinsing of the apparatus was undertaken, the ice which had to be placed in the Dewar's vessel between the brasstube and the walls of the vessel, was prepared. By means of a knife it was scraped off a piece of ice, made by freezing some distilled water; the outer layer of the ice was thrown away because it might be unclean, and great care was taken that the finely scraped ice, which was to be used for the determination of the freezing point, came only in contact with objects which had been washed with distilled water. The ice was always scraped immediately before each experiment.

When the cleaning of the apparatus had been finished some ice was put on the bottom of the Dewar's vessel; the thermometer was placed in the brasstube which was then put so far down in the vessel that the beginning of the divisions was on a level with the brim of the latter, and then the space between the spiral and the walls of the vessel was stuffed with the scraped ice. The vessel *D* was filled

with seawater and put in its place, its stopcocks were opened, and then the water, drop by drop, fell through the narrow tube, to which the lower part of the vessel had been drawn out, into the glasstube *e*. By means of the clip on the tube *d* the speed of the streaming water was regulated so that the supply of fluid to the Dewar's vessel was about 1·5 2 cc per minute. The temperature of the cooling bath was maintained so as to diverge only a few tenths of a degree from the freezing point of the watersample, this being computed from the specific gravity at 0° C. by means of O. Pettersson's observations of the dependence of the freezing point on the specific gravity [1]).

The height of the mercury in the thermometer was now observed at certain intervals. At the beginning of the experiment the mercury was falling quickly, later on slowly, till at least it kept constant; this last temperature then is the freezingpoint.

To avoid errors in the reading on account of the capillarity, the thermometer was tapped a little with a glass-rod before each reading. In order to correct the error arising from part of the mercurial column not being sunk in the fluid, a thermometer was read the bulb of which was placed closely opposite to the middle of the mercurial column not sunk. In order to correct for the outer pressure the height of the barometer was read together with the corresponding temperature.

The thermometer was read with a telescope; sufficient light was produced by means of a glow-lamp and a concave mirror. That the optical axis of the telescope might in each experiment be brought in the same position to the thermometer, a little mirror was fastmed to it by means of an indiarubber band, the back side of this mirror being only slightly coated with silver. Before each experiment the optical axis of the telescope was adjusted perpendicularly to the mirror by placing the telescope in such a position that the image in the mirror of a thread fixed across the object glass was seen to cover the horizontal thread fixed in the telescope.

When the position of the mercury in the thermometer had for some time continued constant with incessant streaming of seawater, the thermometer was read, and the experiment finished. The thermometer was taken out and placed in a mixture of snow and water; the parts of the apparatus were well rinsed with distilled water, and arranged for a new experiment, which was always, after each determination of a seawater sample, an experiment with distilled water to determine the zero of the thermometer.

Before the whole series of experiments was undertaken, the thermometer was again tested. Division and caliber errors were determined by a dividing machine with microscope. The length of degrees was determined by comparison with a standard thermometer, «Tonnelot 4547», belonging to the Polytechnical School, and tested in the Bureau international des poids et mesures. The comparison was undertaken in a Dewar's vessel. Furthermore, the influence of the outer pressure on the indications of the thermometer was determined. The correction arising from the mercurial column not being sunk was determined experimentally by comparing the indications of the thermometer when it was completely sunk in the solution with its indications when it was sunk to the beginning of the scale, consideration being taken to the change of outer pressure following hereof.

Example of a Determination of the Freezing Point.

(From the journal of observation.)

Watersample No. 11.

The experiment commenced at $1^h 45$ p. m.

The temperature of the cooling bath $\div 1{\cdot}7°$. The speed of the streaming water 1·5 cc. per minute.

At $2^h 30$ p. m. Reading $T = 1{\cdot}235$.

At $3^h 07$ p. m. Reading $T = 1{\cdot}233$.

[1]) Otto Pettersson: On the Properties of Water and Ice (Ur "Vega-Expeditionens vetenskaplige lakttagelser" Bd. II. pag. 270).

Height of barometer $B = 734{\cdot}1^{mm}$ (13°).
Temperature at the middle of the mercurial column $t = 11{\cdot}9$.
At $3^h 30$ p. m. Reading $T = 1{\cdot}233$.
$B = 734{\cdot}3^{mm}$ (13°). $t = 12°$.

Distilled water.

The experiment commenced at $4^h 00$ p. m.
At $4^h 45$ p. m. Reading $T = 3{\cdot}020$.
At $4^h 50$ p. m. Reading $T = 3{\cdot}021$.
At $5^h 00$ p. m. Reading $T = 3{\cdot}021$.
At $5^h 30$ p. m. Reading $T = 3{\cdot}021$.
$B = 734{\cdot}5^{mm}$ (13°). $t = 12°$.
The temperature of the cooling bath 0·1°. The speed of the streaming water 1·4 cc. per minute.

From this the freezingpoint for watersample No. 11 is computed.

Watersample No. 11.

Reading of the thermometer	1·233
Correction for caliber error	÷ 0·0017
Correction for outer pressure [1]	+ 0·0027
Correction for the mercurial column not sunk	÷ 0·0033
Correct reading	1·2307

Zeropoint.

Reading of the thermometer	3·021
Correction for caliber error	÷ 0·0028
Correction for outer pressure	+ 0·0027
Correction of the mercurial column not sunk	÷ 0·0069
Corrected zeropoint	3·0140

We have now for watersample No. 11:

Corrected reading	1·2307
Corrected zeropoint	3·0140
Difference	÷ 1·7833
Correction for length of degree	+ 0·0190
Freezingpoint t	÷ 1·764° C.

The freezingpoints thus determined are put down in the following table, corrected to the hydrogen-thermometer, together with the zero-reading answering to each particular freezingpoint, corrected for caliber errors, outer pressure and the temperature of the mercurial column not sunk. In the first column the number of the watersample is stated, in the second the time of reading the freezingpoint, in the third column the freezingpoint corrected to the hydrogen-thermometer, in the fourth column the time of reading the zeropoint, and in the fifth column the corrected zeropoint is stated.

From the column containing the corrected zeropoint readings will be seen that in the course of the first three days the zeropoint has risen 0·003°, then it has again assumed its original value 3·011 which it has kept up during the 5 following days, and then a sudden spring of about 0·04° appears in the zero-

[1] The whole outer pressure is equal to the height of the barometer + the pressure arising from the barometer being sunk in water. The readings of the thermometer are reduced to 760^{mm} mercury pressure at 0° C. and 45° latitude.

point. During the whole period of experiments the quantity of mercury in the bulb of the thermometer was not changed, and during the intervals between the single experiments the thermometer was placed in a vessel with melting ice, sunk to the division to which, during the experiment, it had been sunk in the Dewar's vessel; what the great spring of the zeropoint is owing to must, therefore, remain undecided pro tem. This spring of the zeropoint has, however, not had any influence on the freezingpoints determined here; the repetition of the watersamples No. 7 and No. 21 gave the same result after the spring of

Kol. 1.	2.	3.	4.	5.
No. of the watersample.	Time of reading the freezingpoint.	Freezingpoint.	Time of reading the zeropoint.	Corrected zeropoint.
X	$^{24}/_{I}$ 8h 45 p. m.	−1·923	$^{24}/_{I}$ 11h 00 p. m.	3·011
21	$^{25}/_{I}$ 3h 40 p. m.	−2·015	$^{25}/_{I}$ 5h 35 p. m.	3·011
28	$^{25}/_{I}$ 7h 30 p. m.	−0·562	$^{25}/_{I}$ 8h 40 p. m.	3·012
10	$^{25}/_{I}$ 10h 38 p. m.	−1·246	$^{26}/_{I}$ 0h 20 a. m.	3·012
7	$^{26}/_{I}$ 11h 15 a. m.	−0·984	$^{26}/_{I}$ 0h 55 p. m.	3·013
11	$^{26}/_{I}$ 3h 30 p. m.	−1·764	$^{26}/_{I}$ 5h 30 p. m.	3·014
25	$^{27}/_{I}$ 0h 10 p. m,	−2·207	$^{27}/_{I}$ 2h 45 p. m.	3·011
1	$^{27}/_{I}$ 5h 15 p. m.	−1·834	$^{27}/_{I}$ 9h 00 p. m.	3·011
21	$^{28}/_{I}$ 11h 15 a. m.	−2·018	$^{28}/_{I}$ 1h 35 p. m.	3·010
7	$^{28}/_{I}$ 4h 30 p. m.	−0·983	$^{28}/_{I}$ 6h 20 p. m	3·011
			$^{29}/_{I}$ 4h 00 p. m.	3·010
F. 30	$^{30}/_{I}$ 4h 15 p. m.	−0·787	$^{30}/_{I}$ 5h 50 p. m.	3·047
33	$^{30}/_{I}$ 7h 20 p. m.	−0·286	$^{30}/_{I}$ 8h 45 p. m.	3·047
32	$^{31}/_{I}$ 10h 50 p. m.	−0·144	$^{31}/_{I}$ 1h 00 p. m.	3·047
7	$^{31}/_{I}$ 7h 00 p. m.	−0·986	$^{31}/_{I}$ 9h 30 p. m.	3·047
21	$^{1}/_{II}$ 3h 20 p. m.	−2·019	$^{1}/_{II}$ 5h 20 p. m.	3·046

the zeropoint as before. The only freezingpoint which may be doubted is the one for watersample No. F. 30, which ought to have been repeated if a sufficient quantity of water had been left for another experiment.. As the freezingpoint found for this watersample — which will be shown afterwards — is very much suitable to the formula for the dependence of the freezingpoint on the specific gravity there is reason to suppose that the zeropoint-value used is not very different from the right one.

The drawback in cryoscopic measurements which arises from sudden springs in the position of the zeropoint of the thermometer, has often been observed, especially by Loomis; the consequence of it is that when you determine thousandths of a degree it is necessary to determine the zeropoint immediately after each determination of temperature. The often used proceedings to determine the zeropoint now and then, and to interpolate graphically to the zeropoint answering to a certain time is insufficient. If this method had been used in the present series of experiments the latter would have been quite valueless.

By means of the repetitions which we have of the watersamples No. 7 and No. 21 the mean error in a single observation is found to be for No. 7 $\pm 1 \cdot 7 \times 10^{-3}$ and for No. 21 $\pm 2 \cdot 1 \times 10^{-3}$.

In order to examine if the seawater suffered such alterations of concentration in the Dewar's vessel that the measured freezingpoint did not answer to seawater of the concentration which was determined by the specific gravity when the water was poured into the pycnometer direct from the bottle in which it was kept, a little siphon was placed in a Dewar's vessel, by means of which a pycnometer might be filled with the water enclosing the bulb of the thermometer. When the freezingpoint experiment had lasted so long, that the temperature had become constant, the water, enclosing the bulb of the thermometer was, by means of the siphon, led into the pycnometer with the same speed with which it entered the vessel through the brass-spiral, which might be seen from the fact that the surface of the

fluid in the Dewar's vessel was steadily keeping at the same height. The result of these determinations of specific gravity was for watersample No. 7:

Specific gravity when the water was taken direct from the bottle.....	1·0147062
Specific gravity when the water was taken from Dewar's vessel	1·0146984
Difference...	0·0000078

The greatest deviation between repeated determinations of specific gravity of the same watersample, when the water was taken direct from the bottle, was 0·000002, while the difference here is 0·0000078. This difference may, however, be explained; it was, namely, exceedingly difficult to make the water run into the pycnometer with the speed with which it entered the Dewar's vessel; the pycnometer had to be filled by jerks, and so part of the fluid lying above the bulb of the thermometer came into the pycnometer. Near the surface in the Dewar's vessel the solution may, indeed, be a little attenuated by the melting of ice caused by the heat which is led through the free surface; but the experiment shows at any rate that the alterations of concentration are not so great as to be of any importance in the present case.

3. Determinations of Specific Gravity.

In order to determine the specific gravity at 0° C. of the watersamples, the same method and the same apparatus were applied as applied by Mr. MARTIN KNUDSEN[1]) in the constant determinations for the revision of the hydrographic tables, so these determinations will not be mentioned further here.

4. Relation between the Freezingpoint and the Specific Gravity.

In the following table are noted corresponding values of the freezingpoint t and σ_0, σ_0 being equal to 1000 (s_0-1), where s_0 is the specific gravity at 0° C. in relation to distilled water at 4° C.

No. of the watersample.	Freezingpoint t° C.	σ
Distilled water	÷ 0·000	÷ 0·13
32	÷ 0·144	+ 2·09
33	÷ 0·286	4·24
28	÷ 0·562	8·48
F. 30	÷ 0·787	11·76
7	÷ 0·984	14·71
10	÷ 1·246	18·66
11	÷ 1·764	26·01
1	÷ 1·834	27·01
X	÷ 1·923	28·35
21	÷ 2·017	29·66
23	÷ 2·207	32·30

From these values for t and σ_0 has by the method of least squares been found the following relation between t and σ_0:

$$t = \div 0{\cdot}0086 \div 0{\cdot}064633\,\sigma_0 \div 0{\cdot}0001055_0\sigma_0{}^2.$$

In the determination of the constants in the formula above by the method of least squares all weights are taken equal, as the mean error in the single determinations must be supposed to be the same.

[1]) Berichte über die Konstantenbestimmungen.

In the table below the differences $t_{observed} \div t_{computed}$ are noted from which may be seen that the formula suits sufficiently well.

No. of watersample	Distilled water	32	33	28	F. 30	7	10	11	1	X	21	23
$t_{observed} \div t_{computed}$	0·000	+ 0·001	÷ 0 001	+ 0·002	÷ 0·004	÷ 0·001	+ 0·005	÷ 0·003	÷ 0·002	+ 0·003	+ 0·002	÷ 0·001

In «On the Properties of Water and Ice» p. 270 Otto Pettersson communicates a series of corresponding values for the freezingpoint and the specific gravity. The proceedings in order to determine the freezingpoint were the following: The freezingpoint of a considerable quantity of water was first roughly ascertained, then it was slowly cooled to about 0·2 or 0·3° C. below its normal freezingpoint, then a crystal of snow was thrown into the vessel and the maximum of temperature observed by a Geissler thermometer. During the whole process the water was constantly stirred. Pettersson gives the following relations between the freezingpoints and the specific gravities:

Freezingpoint $t°$ C.	σ_0	$t_{computed}$	$t_{observed} \div t_{computed}$
÷ 1·895	27·1	÷ 1·838	÷ 0 057
÷ 1·715	24·4	÷ 1 648	÷ 0·067
÷ 1·025	14·8	÷ 0 988	÷ 0·037
÷ 0·85	12·2	÷ 0·813	÷ 0·037
÷ 0·715	10·4	÷ 0·692	÷ 0·023
÷ 0·27	4·1	÷ 0 275	+ 0·005

If we compute the freezingpoint according to Pettersson's values for σ_0 from the formula mentioned above we get the column $t_{computed}$. If the differences $t_{observed} \div t_{computed}$ are formed we see that the disagreement between the relation found here and Pettersson's determinations is considerable; the freezingpoint lies lower than it ought to do according to the formula; the differences increase with the depression and reach as far as about 0·07° C.

5. Determination of σ_0 for the sea-water the freezingpoint of which coincides with the temperature at which σ_t is the maximum.

In order to determine the temperature in which the specific gravity of the seawater is the maximum, we use the formula found by Martin Knudsen[1]).

where

$$\sigma_t = \Sigma_t + (\sigma_0 + 0{\cdot}1324)\,[1 - A_t + B_t\,(\sigma_0 - 0{\cdot}1324)],$$

$$\Sigma_t = \div \frac{(t - 3{\cdot}98)^2}{503{\cdot}570} \cdot \frac{t + 283}{t + 67{\cdot}26},$$

$$A_t = t\,[4{\cdot}7867 - 0{\cdot}098185\,t + 0{\cdot}0010843\,t^2].\ 10^{-3},$$

$$B_t = t\,[18{\cdot}030 - 0{\cdot}8164\,t + 0{\cdot}01667\,t^2].\ 10^{-6}.$$

[1]) Hydrographische Tabellen. p. IV.

If σ_t is differentiated as to the temperature t we get:

$$\frac{d\sigma_t}{dt} = \frac{d\Sigma_t}{dt} - (\sigma_0 + 0{\cdot}1324)\frac{dA_t}{dt} + (\sigma_0{}^2 - 0{\cdot}1324^2)\frac{dB_t}{dt},$$

where

$$\frac{d\Sigma_t}{dt} = \frac{t-3{\cdot}98}{t+67{\cdot}26}\left[\frac{215{\cdot}74}{503{\cdot}57}\cdot\frac{t-3{\cdot}98}{t+67{\cdot}26} - \frac{2}{503{\cdot}57}(t+283)\right],$$

$$\frac{dA_t}{dt} = 10^{-3}[4{\cdot}7867 - 0{\cdot}19637\,t + 0{\cdot}0032529\,t^2],$$

$$\frac{dB_t}{dt} = 10^{-6}[18{\cdot}030 - 1{\cdot}6328\,t + 0{\cdot}05001\,t^2].$$

If the differential quotient is put at $\frac{d\sigma_t}{dt} = 0$, we get the condition of maximum:

$$\frac{d\Sigma_t}{dt} - (\sigma_0 + 0{\cdot}1324)\frac{dA_t}{dt} + (\sigma_0{}^2 - 0{\cdot}1324^2)\frac{dB_t}{dt} = 0;$$

if the expressions for $\frac{d\Sigma_t}{dt}$, $\frac{dA_t}{dt}$, and $\frac{dB_t}{dt}$ are substituted here and t is eliminated between the equation got in this way and the equation between the freezingpoint t and σ_0 found above:

$$t = -0{\cdot}0086 - 0{\cdot}064633\,\sigma_0 - 0{\cdot}0001055_0\,\sigma_0{}^2,$$

we get $\sigma_0 = 19{\cdot}84$, to which answers $t = -1{\cdot}332°$ C.

For σ_0 equal 19·84, to which answers a quantity of chlorine equal to 13·665 ‰ and a salinity equal to 24·695 ‰, the freezingpoint, $-1{\cdot}332°$ C. coincides with the temperature in which σ_t is the maximum.

In «Grunddragen af Skageracks og Kattegats Hydrografi» by Pettersson and Ekman it is said that for the seawater the freezingpoint of which coincides with the temperature answering to the maximum of density, σ_t must be between 19 and 20 and the freezingpoint lie below $-1°$, which has also here proved to be right.

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ON THE DETERMINATION OF CHLORINE IN SEA-WATER

AND

EXAMINATION OF THE ACCURACY WITH WHICH KNUDSEN'S PIPETTE MEASURES A VOLUME OF SEA-WATER

BY

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At the request of Docent M. KNUDSEN, I have made an investigation of the exactness which may be gained as to determinations of chlorine in sea-water[1]), if we titrate the chlorine with a solution of silver-nitrate with chromate of potash as the indicator, and use standard water — that is sea-water with exactly known contents of chlorine — for the adjustment of our solution of silver.

According to analytical manuals, as MOHR's Lehrbuch der Titrirmethode (Classen's edition), LUNGE's chemisch-technische Untersuchungsmethoden, and FRESENIUS's Quantitative Analysis, this method suffers from a systematical error: in order to produce the red tint to which we titrate, we are obliged to add an excess 0·1—0·2 cc solution of silver, when we work with $^1/_{10}$ normal fluids. In his description of the hydrographic tables[2]), Mr. KNUDSEN has estimated this systematical error at being at the highest 0·05 ‰ in the salinity which corresponds to about 0·025 ‰ in the amount of chlorine. It would be of interest to have this matter examined more thoroughly, and on the whole the principal point is to decide whether it is possible to obtain a greater exactness than hitherto in the determinations of the amount of chlorine, without, however, impeding the separate analysis.

The way in which the quantity of chlorine in sea-water is determined in the Danish Hydrographic Laboratory is the following. With a pipette of about 15 cc., provided with a three-way stopcock above — a socalled KNUDSEN's pipette — a certain volume of sea-water is taken. (The pipette is taken out slowly, at the very moment of its having run empty; and its stopcock is greased with glycerine, the besmearing of the inner surface of the pipette being avoided in this way.) A few drops of an 8 % solution of chromate of potash are poured into the sea-water, and to this is added from a burette about $^1/_4$ normal solution of silver-nitrate, towards the close with fast stirring (whipping), until a part of a drop can make the fluid red, even if it has been carefully stirred before the addition. The burette is furnished with head-graduations, at about 2 cc, which indicate, approximately, the contents of chlorine in the sample in weight pro mille. Everywhere hereafter when quantities of solutions of silver-nitrate are mentioned, these burette-graduations of about 2 cc are taken as units. The burette, whose graduation lines are very fine, is read by means of a so called ball-float; it is filled with a solution of silver-nitrate from an elevated large bottle through a stopcock on the burette. For the very saline water of the Atlantic Ocean are also used ball-burettes without floats and with a greater distance between the graduations. The red tint of the fluid, which must be said rather to appear as a soiling of the pure light-yellow colour of the chromate of potash, does not keep, on a stirring for a lengthened period. Stirring a dozen times after the addition does not, however, do any harm. The tint must stand this. Then the burette must be read immediately when the transition point has been found. A titration of standard water is executed in the same way, and by means of the little difference between the quantity of silver-nitrate applied and the

[1]) As to the definition of "mass of chlorine in sea-water" see S. P. L. SØRENSEN, Ph. d. Kgl. danske Vid. Selsk. Skr., 6. R., nat. og math. Afd. X. 1. p. 97—98.

[2]) Wiss. Meeresuntersuch. Abtheilung Kiel. Neue Folge. Band 6. p. 164.

known quantity of chlorine in the standard water we find (see KNUDSEN's hydrographic tables) how much has to be added to the quantity of silver-nitrate, which was used for the sea-water sample, in order to get the contents of chlorine of the sea-water in weight pro mille.

The errors committed in such a determination of chlorine are the following. First, exactly the same volume of sea-water is not each time taken with the pipette. Secondly, the determination of the volume of silver-nitrate applied is encumbered both with reading-errors and with running-off-errors, that is the errors originating in the fact that a different volume of solution of silver remains adhering to the walls of the burette; and last but not least with graduation-errors (caliber-errors). Further, errors occur when the sea-water and the standard water have not the same temperature, and if the solution of silver-nitrate changes its temperature between the titration of the sea-water and that of the standard water. The error originating in the change of the composition of the solution of silver-nitrate is so insignificant that it need not be taken into account, if only care is taken and the last remainder of the solution in the bottle is not used. Nor will we take into account the error arising from inaccurate knowledge ot the quantity of chlorine in the standard water (it is difficult to discern how great the error may be, but probably it is only 1:10000 of the whole quantity of chlorine). Another error occurs because we are obliged to add a surplus of the solution of silver-nitrate in order to get a visible red tint. For the sake of completeness is to be mentioned that the rounding off in the hydrographic tables produces a little error.

We shall look a little more fully at each of these sources of errors.

In order to determine the variability of the volume of sea-water which is taken with a KNUDSEN's pipette of 15 cc., a series of trials was made in which the taken volumes were weighed:

When the pipette was taken up, as soon as it had run out, it took of distilled water of 14° C.:

15·592 gr.; 15·592 gr.; 15·588 gr.; 15·591 gr.; 15·591 gr.; 15580 gr.

mean number: 15·589 gr. answering to 15·616 cc. mean error: 0·0046 cc.

Of sea-water with 18·89 ‰ of chlorine, 16° warm was taken:

16·000 gr.; 15·993 gr.; 15·993 gr.; 15·997 gr.; 15·991 gr.;

mean number: 15·995 gr. answering to 15·613 cc. mean error: 0·0037 cc.

If we wait half a minute before we take up the pipette, we get for distilled water of 14°:

15·599 gr.: 15·601 gr.; 15·596 gr.; 15·596 gr.

mean number: 15·598 gr. answering to 15·625 cc. mean error: 0·0025 cc.

Besides the accidental errors, the effects of which may be diminished by repeating the trial, a systematieal error is found in the pipette. Namely: the same volume of a strong and a diluted saline solution does not remain adhesive to the walls of the pipette. According to the above mentioned trials, the difference, however, is only 0·003 cc., when we compare distilled water and sea-water with about 19 ‰ chlorine.

In an analysis-result of a ‰ chlorine the pipette error will work with a mean error: $0{\cdot}0042 \cdot \frac{a}{15{\cdot}6} = a \cdot 0{\cdot}00027$, and the systematical error will be: about $\frac{19{\cdot}3 \div a}{19{\cdot}3} \cdot \frac{0.003}{15{\cdot}6} \cdot a = 0.00001 \cdot (20 \div a) \cdot a$ (19·3 is the chlorine contents of the standard water).

The mean error which appears at the reading of the burette may be reckoned at: $0{\cdot}006 \cdot \frac{1}{\sqrt{3}} = 0{\cdot}0035$, when we suppose that values as $18{\cdot}45 \pm 0.006$ are all rounded to 18·45. (I have reckoned with 0·006 and not with 0·005, because we do not always round to the right side.) The setting on the zero line, however, is a little more exact. The mean error here may perhaps be estimated at 0·0025. The running-off error on the burette may, proximately, be supposed to be as great in proportion to the quantity of fluid as the error in the pipette. So it is: $a \cdot \frac{0{\cdot}0042}{15{\cdot}6} = a \cdot 0{\cdot}00027$ (a is as above the chlorine contents of the analysis.

The systematical error which arises from the fact, that the adhering quantity of fluid is not proportional to the consumed volume of solution of silver, will be removed if we have calibrated our burette by weighing the quantity of solution of silver which runs out from the zero line to the different graduation lines, and have waited the same time with the reading as we did at the common titration. If we do not examine our burette very carefully and in this very way, the mean error will easily reach 0·01 on account of the inaccurate correction. But by an accurate and repeated calibration we are enabled to reduce this error a good deal.

A difference of two degrees in the temperature of the sea-water and the standard water (18° to 20°) gives a change in the result of about 0·05 % of the whole value, and an alteration of the temperature of the solution of silver from 18° to 20° acts with a force of 0·04 %. The latter error may, however, be disregarded because, mostly, it lessens the former. If, at the same time, a difference of two degrees in the temperature of the sea-water and the standard water is supposed to be the greatest possible, and if the difference has, equally frequently, all the values between 0 and 2, the mean error which is caused by the temperatures altering the specific gravities of the solutions will be: $a \cdot 0{\cdot}0005 \cdot \frac{1}{\sqrt{3}} = a \cdot 0{\cdot}00030$.

The mean error caused by the rounding off in the hydrographic tables is: $0{\cdot}005 \cdot \frac{1}{\sqrt{3}} = 0{\cdot}003$.

Finally we have to mention the error caused by the surplus of solution of silver which is necessary in order to produce the change of colour to which is titrated. Having tried different other methods to determine the quantity of this surplus, I abode by the following proceeding. To the reddish mixture of chloride of silver and liquid from a completed titration were added 5 or 6 drops of 10 % nitric acid (some more when there was much chromate of potash) and then lead-nitrate was added in surplus. By this all the chromic acid was precipitated as salt of lead. After a delay of 10 or 15 minutes a filtration took place, and the quantity of silver in the filtrate was determined, according to VOLHARD's method, by titration with $^1/_{50}$ normal solution of sulphocyanate of potassium and with ferrinitrate as the indicator. This titration was always undertaken by incandescent light, as it was impossible to see the change of colour sufficiently distinctly by daylight. That the method was efficient was tried by determining the quantity of silver in a thin solution ot silver-nitrate, partly direct by VOLHARD's method, and partly after adding chromate of potash according to the method mentioned above.

According to VOLHARD were found in 20 cc.: 0·0158 and 0·0165 burette units of solution of silver
and according to the method mentioned above: 0·0158 — 0·0161 — — —

This quantity of silver-nitrate being of similar quantity as the surplus of silver-nitrate by the titration of sea-water, these four results give an idea of the exactness in the determination of this surplus.

The table on the following page will show how the surplus of solution of silver-nitrate by a titration depends on the quantity of the chromate of potash and on the quantity of chlorine.

I want to emphasize that these surplusses were found by titrations where we had ceased to add solution of silver-nitrate, when a fractional part of a drop gave a tint which held, even when the fluid was stirred for half a score of times. It had, of course been carefully stirred before the little fraction of a drop was added. The titrations were made by different persons and both by daylight and by incandescent light, but these differences had no particular influence on the results. The electric light made it, indeed, a little easier to see the transition, but did not alter the quantity of the surplus so much that it could be perceived.

When two drops of chromate of potash are used, the surplus is on an average:

for 17—18 ‰ of chlorine 0·020 with a mean error of 0·004,
- 10—12 ‰ - — 0·017 — — 0·001.

This quantity of chromate of potash was formerly used at the laboratory, but it seems to be better to take some more. When we use 5 or 6 drops the average value of the surplus is:

for 16·9 ‰ chlorine 0·011 with a mean error of 0·0028,
- 4·9 ‰ — 0·005 — — 0·0028.

Added of $K_2 Cr o_4$ solution:	1 drop [1]		2 drops		4 drops		5 drops		6 drops		8 drops		20 drops	
Quantity of solution of silver:	Used for the titration	Surplus of this	Used for the titration	Surplus of this	Used for the titration	Surplus of this	Used for the titration	Surplus of this	Used for the titration	Surplus of this	Used for the titration	Surplus of this	Used for the titration	Surplus of this
18—19 ‰ Cl....	18·45	0·016	19·37	0·022										
			18·34	0·019	18·50	0·010	.....	.....	18·61	0·009				
			18·14	0·019										
	17·74	0·020	18·06	0·018	.....	.....	.....	.....	.....	.....	18·06	0·011		
17 ‰ Cl.....			17·22	0·025 [2]										
			17·21	0·022 [2]										
			16·89	0·025*	.....	.....	16·885	0·013*	16·885	0·008*	.....	.....	16·88	0·009*
			16·875	0·013*	.....	.....	16·885	0·012*	16·885	0·007*	.....	.....	16·875	0·004*
							16·88	0·013*						
							16.875	0·010*						
							16·87	0·015*						
10—12 ‰ Cl....			12·18	0·016										
			11·33	0·018 [2]										
			10·67	0·017										
5 ‰ Cl.....							4·90	0·007						
							4·885	0·003						

[1] A drop contains 0·006 Gr. $K_2 Cr O_4$.

[2] These surplusses are determined in a somewhat different way.

It is evident that the systematic error which is due to this surplus will be nought, when the sea-water and the standard water have the same composition. It grows with the decreasing salinity of the sea-water.

When we use 5 or 6 drops of chromate of potash the surplus for standard water with 19·3 ‰ chlorine will be about 0·012. If now the surplus for 4·9 ‰ chlorine was $0{\cdot}012 \cdot \frac{4{\cdot}9}{19{\cdot}3}$ = about 0·003, the systematic error would also be nought for sea-water with these contents of chlorine. It is, however, 0·005, and so the systematic error will be 0·002 for 4·9 ‰ contents of chlorine.

When we use 2 drops of chromate of potash we find, by a similar consideration, that the systematic error for water with 10—12 ‰ contents of chlorine will be $0{\cdot}017 \div 0{\cdot}020 \cdot \frac{11}{19{\cdot}3} = 0{\cdot}005$; and it will certainly be less — about 0·003 — when we use 5—6 drops of chromate of potash.

The surplus of solution of silver-nitrate which is necessary in order to give the red tint, is not owing to the stuffs which are found in sea-water besides sodium-chloride, and the quantity of the surplus does not depend on them either. Even if a pure solution of sodium-chloride is titrated, the same surplusses are used. The surplusses which in the table are marked with an asterisk arise from titrations of a pure solution of sodium-chloride.

I have tried how the surplus varies when there is a somewhat greater quantity on hand of some of the stuffs which are found in sea-water in smaller quantities. A solution of sodium-chloride to which were added the mentioned quantities of foreign matters, gave the following surplus:

Added matters:	Solut. of silver-nitrate employed:	Surplus thereof:
5 drops of $K_2 Cr O_4$; 1 cc. 2% $Na HC O_3$	16·88	0·018
— 2 cc. —	16·89	0·017
— 1 cc. 4% $Na_2 CO_3$	16·89	0·023

Carbonate of sodium and acid carbonate of sodium have, consequently, even in pretty considerable quantities, only an insignificant influence. Not so with caustic soda. If we titrate the above mentioned solution of salt after having added 1 cc. 0·4 % soda we get a gradual transition between 16·91 and 17·0 solution of silver employed.

The different acting of these stuffs may be explained by the dissolubility of the corresponding silver combinations.

Instead of chromate of potash we might use arseniate of sodium for the indicator. According to LUNGE's Handbuch der chemisch-technischen Untersuchungsmethoden we use a smaller surplus of solution of silver with this indicator than with chromate of potash. I have found that the surplusses were almost equally large with both. With 1 cc. of a 10 % solution of arseniate of sodium as the indicator in titration by daylight of a solution of sodium-chloride with about 17 ‰ chloride we used the following surplus of the solution of silver: 0·011; 0·004; 0·013. The transition was, however, bad both with $^1/_5$ and with 5 cc. of arseniate of sodium. But it is much more difficult even by daylight, which is best, to see the transition, when you use arseniate of sodium than it is when you use chromate of potash; and the latter is therefore to be preferred.

When we add the little systematic error which arises from the pipette, to the one which is due to the necessary surplus of the solution of silver, we get as the total systematic error in the chloride titration of the laboratory (by using 6 drops of chromate of potash): 0·000 for 19·30 ‰ Cl. + 0·004 for 11 ‰ Cl., + 0·002 for 5 ‰ Cl. For a very low quantity of chloride it will probably be about 0·002.

When we calculate the table of the graduation errors of our burette so that the error for 19·3 is nought, we only need to add the above mentioned numbers — and the numbers interpolated between them — to the values of the table to get the correction which is to be added to the result of the analysis (or to the reading of the burette at the titration of sea-water).

The sources of errors with which a corrected result of analysis is encumbered have the following sizes indicated by their mean errors.

From the titration of standard water the following errors arise:

pipette error	$0.00027 \cdot 19{\cdot}3 = 0{\cdot}0052$
error of adjustment on the burette	0·0025
reading error	0·0035
running off error	0·0052
mean error from the surplus	0·0028

From the titration of sea-water arise:

pipette error	$0{\cdot}00027 \cdot a$
error of adjustment on the burette	0·0025
reading error	0·0035
running off error	$0{\cdot}00027 \cdot a$
mean error on account of inaccurate calibration (except quite near 0 and 19·3 ‰ Cl.)	0·0100
mean error from the surplus	0·0028

To this must be added:

temperature error	$0{\cdot}00030 \cdot a$
rounding off error from the tables	0·0030

From these numbers is calculated that the mean error in an analysis of sea-water is about $0{\cdot}015 \cdot (1 + a^2 \cdot 0{\cdot}0005)$, that is about 0·015—0·018. It stands to reason that we give no consideration to the errors which ought not to be committed, but which are not always avoided, for instance sprinkling by the adding of the solution of silver, unclean apparatus and the like.

From this result may be concluded that the probability is that two thirds of the analysis effected will differ with less than 0·15—0·018 ‰ from the real value. But this, of course, only stands for great numbers of trials, where certain of the trial conditions have not steadily been kept unaltered.

Though I feel inclined to think it unnecessary, I shall, however, by way of making sure, emphasize that the values which I have indicated for the mean errors are only founded on an estimate, and that for instance a value as 0·0028 might perhaps more correctly be 0·0023 or 0·0033.

By means of this summary of the sources of errors of the method and of their size it is possible to see how to obtain a greater accuracy. As it will be seen, the surplus of the solution of silver, which is used in a titration, does not play so prominent a part neither in the systematic errors nor in the casual ones, that it can pay to take measures for lessening it, for instance by using a particular sort of artificial light (sodium-light). If we want to have the determinations of chloride in sea-water executed more accurately, we must direct our attention to other points. We shall especially be able to gain a somewhat greater accuracy by determining the graduation errors of our burette more accurately. Furthermore, it will be of a little, though not much avail if we rinse our pipette with distilled water after its having run empty, and that the burette, as well as the pipette, is at the top provided with a three-way stopcock, greased with glycerine. This is proposed by Mr. KNUDSEN. In this way the adjustment to the zero-mark is not only avoided, but the burette will probably not so easily get greasy. The grease gathers on the surface which here lies outside the measuring space of the burette. But all these improvements could not even together lessen the mean error to the half. A more considerable increase of the accuracy will probably only be obtained by going over to weight titration.

The greatest annoyance in the titration with chromate of potash as the indicator, especially to unexercised people, is that even a strong tint may disappear on fast stirring for some time. This circumstance has already been mentioned, and it was told how to avoid this difficulty. But what is, properly speaking, the reason of the disappearing of the red tint? It may be considered as a matter of certainty that the red tint arises from finely spread chromate of silver. It might, therefore, be imagined that the chromate of silver was decomposed because the fluid contained a scarce quantity of an acid the silver salt of which was less dissolvable than that of chromic acid, but as the tint does not disappear on stirring, if the reddish fluid is first decanted from the chloride of silver, this possibility is excluded. What happens on stirring probably is: that the red chromic silver oxide is clotting together with the chloride of silver and is enveloped by it. A certain quantity of colouring matter will colour a fluid in which it is suspended much stronger than it will colour a powder in which it is mixed. For in the fluid we can see all the colouring particles, while in the pulverulent mixture we can only see an inconsiderable part of them. Of circumstances which favour this point of view may be mentioned that if we make the surplus of silver rather large, for instance add 2 or 3 drops, when the proper point of transition has been found, we may by sufficient stirring get the fluid pure yellow, but the chloride of silver assumes a distinct reddish tint.

It also appears that a mixture on fast stirring contains most of its surplus of silver in the sediment. In some determinations of the surplus of silver separately in the chloride of silver and in the decanted fluid the following results were found:

Silver-nitrate used for the titration	Surplus thereof		The used quantity of chromate of potash	Remarks
	in the fluid	in the sediment		
16·885	0·004	0·004	6 drops	The sediment looked uncoloured.
16·875	0·003	0·004	—	—
16·875	0·009	0·004	2 drops	—
16·88	0·004	0·016	20 drops	A little more silver-nitrate than commonly had been added, but still the sediment was not after stirring so red that the colour could be seen.
16·91	0·005	0·030	6 drops	The sediment was reddish after the stirring.

In the preceding paper some determinations were made as to the accuracy with which by means of KNUDSEN's pipette we could measure a series of fluid volumes of the same size, and we found a mean error of about 0·004 cc. for a pipette which held about 15 cc., and which ran empty in about 30 seconds, when we raised the pipette slowly immediately after its having run out.

The influence of this mean error on the accuracy of the results of the titration is only slight. But this error might perhaps be essentially greater for certain unclean water sorts which for instance contained mire, plankton, and the like. So we took a series of determinations of the weights of fluid which a Knudsen pipette measured of about 40 different water-samples, which were taken round about in the Danish waters in the beginning of the month of May 1903. The pipetting was done quite as it is done in the titrations of chlorine at the Danish Hydrographic Laboratory, and by the same person that executes these determinations. The pipetted fluid was placed in a CHAMBERLAND flask and then weighed. The specific gravity at the temperature of the water was calculated from the quantity of chlorine found in the usual way by means of KNUDSEN's hydrographic tables. And then the volume of the measured fluid was calculated hereof.

The results are entered in table 1. The two first heads indicate from whence the water comes[1]), the third indicates the temperature of the water during the measuring, the fourth indicates the salinity in weight pro mille, and the fifth indicates the volume in cc. which the pipette has measured.

Table 1.

No.	Station	Depth in meter	Temperature	S ‰	Volume	Remarks
1	Da 11	7·5	14·5	21·46	15·829	
2	» 18	15	»	25·95	15·825	
3	» »	20	»	32·20	15·826	
4	» »	30	»	33·10	15·810	
5	» »	40	»	33·82	15·830	
6	» »	50	»	34·145	15·826	
7	» »	12·5	»	22·09	15·833	
8	» 19	0	»	11·26	15·822	
9	» »	5	»	13·29	15·822	
10	» 4	50	17·5	34·81	15·829	
11	» »	40	»	34·76	15·831	
12	» »	30	»	34·09	15·833	
13	» »	20	»	33·01	15·831	
14	» »	15	»	32·34	15·829	
15	» »	10	»	31·85	15·834	
16	» »	5	»	25·12	15·826	
17	» 5	0	»	22·13	15·825	
18	» »	82	»	34·91	15·827	
19	» »	75	»	34·91	15·827	
20	Da 5	50·5	17·5	34·86	15·828	
21	Gjedser Rev	11	20·2	14·28	15·835	
22	»	»	»	14·71	15·831	
23	»	»	»	13·71	15·825	
24	»	»	»	10·91	15·829	
25	»	»	»	12·11	15·829	
26	»	»	»	14·94	15·834	
27	»	»	»	15·15	15·825	
28	»	»	»	9·92	15·829	
29	»	»	»	8·79	15·829	
30	Da 12	34	»	34·65	15·834	
31	» 10	55	»	34·80	15·832	Considerable sediment in the water sample
32	» 11	50	»	34·695	15·837	
33	Kobbergrund	17	»	32·38	15·834	
34	Destilled	water	19·2	0	15·827	
35	»	»	»	»	15·833	
36	»	»	»	»	15·820	
37	»	»	»	»	15·819	
38	Standard water VI a		»	34·97	15·813	

[1]) As to the indications, see: Bulletin publié par le bureau du conseil permanent international pour l'exploration de la mer. Année 1902—1903. No. 2.

As the mean value we get that the pipette measures 15·828 cc. The mean error on a single determination is 0·0058 cc. This value is certainly greater than the earlier found (about 0·0040), it is however of the same order of value. It must also be remembered that the determinations which are the basis of the new value are less comparable than those which are the basis of the old determination. It is worth observing that even the three samples which are most fouled with solid particles, No. 30, 31 and 32 only give a mean error of 0·0066 cc.

When we divide the determinations according to temperature and salinity and form the mean value of the determinations which fall under each interval, we get the following table, where the number in parentheses indicates the number of determinations which come under the mean.

Table 2.

	0 ‰ S.	5—15 ‰ S	15—30 ‰ S	30—35 ‰ S
14·5° C...	.....	15·822 (2)	15·829 (3)	15·823 (4)
17·5° C...	.....	.....	15·825 (2)	15·830 (9)
19·2—20·2° C...	15·825 (4)	15·830 (8)	15·825 (1)	15·830 (5)

It appears from this table that the temperature and the salinity do not exercise any systematic influence of greater significance on the volume of fluid which remains adhering in the pipette.

As the result of the determinations it consequently appears that the pipette error in the uncleaner sea-water samples does not seem to be of essentially greater importance than else. But on the other hand it must be remembered that a mean error of 0·0058 cc. in a rather great number of determinations may very well be consistent with rather great deviations in single determinations. In the 38 determinations on hand there are even two, No. 4 and No. 38, where the error is three times as great. In these cases the pipette error would have altered the result of the titration with two units in second decimal place.

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